



# Carbon supported Pd–Cu catalysts for highly selective rearrangement of furfural to cyclopentanone



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## ABSTRACT

The aqueous phase hydrogenation of furfural to cyclopentanone was investigated using carbon supported Pd–Cu catalysts prepared by various methods. The most active and selective Pd–Cu catalysts were obtained using electroless plating procedure of deposition of copper in the presence of tartrate carboxylate ligands. It is an alternative and promising way to deposit metal nanoparticles onto the surfaces of porous solid supports. As the XRD data revealed in these catalysts beside metallic palladium with the particle sizes 6.8 nm the copper exist mainly in Cu<sup>+</sup> oxidation state as Cu<sub>2</sub>O and the metallic copper is practically absent. The selectivity to cyclopentanone was enhanced gradually by the addition of 3, 5 and 10 wt% of copper precursor on the pre-reduced 5%Pd/C catalyst. An appropriate Pd<sup>0</sup> and Cu<sup>+</sup> distribution is presumed to be a key in gaining excellent catalytic activity. Under reaction conditions where mass-transfer effects were eliminated the furfural conversion about 98% and cyclopentanone yield 92.1 mol% were achieved using only 1 wt% concentration of 5%Pd–10%Cu/C catalyst and reaction time 1 h. According to the proposed mechanism the dominant parameters responsible for reaching very high selectivity of cyclopentanone are (i) very high yield of primary formed furfuryl alcohol and (ii) higher rate of its subsequent conversion to cyclopentanone via the pathway not involving 4-hydroxy-2-cyclopentenone as the main intermediate.

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## 1. Introduction

Furfural is the product of acid-catalysed dehydration of xylose, which is a main component of hemicellulose. The current commercial processes uses agricultural waste, e.g. corn cobs as raw materials and potential resources include black liquor from the pulp processes. Hydrogenation of furfural leads to the attack of C=C or/and C=O bonds, and the products are furfuryl alcohol, 2-methylfuran and tetrahydrofurfuryl alcohol [1,2]. Since the most metal catalysts can hydrogenate both C=C and C=O bonds, the control of relative activity in C=O/C=C furfural hydrogenation is one of the most important theme of the design of hydrogenation catalysts [3]. Hydrogenolysis of C–O bond in ethers such as tetrahydrofuran ring proceeds only over limited catalysts. One typical example is the hydrogenolysis over Rh or Ir catalysts modified with ReOx [4]. In the presence of strong acid catalysts furfural is easy polymerized

[5]. The polymerization or oligomerization reactions are usually side-reactions in many processes of furfural conversion. The partial hydrogenation product of furfural, furfuryl alcohol is also very easy polymerized, or in the presence of very strong acids rearranged to levulinic acid (4-ketopentanoic acid) or to its esters, when the reaction is performed in alcohols as solvents [6].

Recently, we have demonstrated entirely new method of rearrangement reaction of furfural [7,8] and furfuryl alcohol [9], which in one-step produces cyclopentanone with very high yield and selectivity. This type of rearrangement reaction proceeds only in aqueous media in the presence of hydrogen and suitable metal catalyst. Various supported and bulk types of metal catalysts (e.g. Pt, Pd, Ru, Ni, Raney Ni types) were tested under different reaction and concentration conditions. Later, other authors used for the furfural rearrangement to cyclopentanone Cu–Ni/SBA-15 [10], Cu–Co [11], CuZnAl [12] and CuNiAl hydrotalcite [13] type catalysts, and for the conversion to cyclopentanol CuMgAl hydrotalcite [14] and Ni/CNT [15] catalysts.

Cyclopentanone is a versatile compound used for the synthesis of fungicides, pharmaceuticals, rubber chemicals, and flavour

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and fragrance chemicals [16]. Potentially, it can be used for preparation of polyamides [17], C<sub>15</sub>–C<sub>17</sub> diesel or jet fuels [18] and polyolefin stabilizers [19]. Cyclopentanone can be prepared by the catalytic vapour-phase cyclization of 1,6-hexanediol [20] or adipic acid esters [21–23] or by the liquid phase oxidation of cyclopentene with nitrous oxide [24,25].

Herein, we report the catalytic conversion of furfural to cyclopentanone, applying supported Pd and Pd–Cu catalysts. The reason for incorporating Cu into the Pd catalysts was that copper-based catalysts have been the most widely used to achieve selective hydrogenation of the C=O bond while leaving the C=C bonds in the furan nucleus intact [26]. The main objective was to study the influence of copper in bimetallic Pd–Cu catalysts prepared by different methods on the activity and selectivity of cyclopentanone formation. For deposition of copper electroless plating method was successfully applied. This procedure producing particles with uniform size and shape is widely used in electronics for deposition of metallic layers on semiconductors or dielectrics [27,28]. In addition, various parameters such as catalyst composition, speed of stirring, catalyst loading, and hydrogen pressure and reaction temperature were studied to optimize the furfural conversion to cyclopentanone and to elucidate the mechanism of this new rearrangement reaction.

## 2. Experimental

### 2.1. Materials

Furfural (98%), furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (98%), cyclopentanone (99%), cyclopentanol (99%), 2-cyclopentenone (98%), tetrahydrofuran (98%), methanol (99%), *n*-butanol (98%), palladium chloride, CuSO<sub>4</sub>·5H<sub>2</sub>O and formaldehyde (37%) were purchased from Sigma–Aldrich. Furfural before experiments was purified by vacuum distillation and stored at –15 °C. Activated charcoal Norit (1030 m<sup>2</sup> g<sup>–1</sup>) was from Fluka. Commercial nickel type catalyst G-134A was from Süd-Chemie.

### 2.2. Catalyst preparation

Monometallic palladium and copper catalysts supported on activated carbon were prepared by standard impregnation method using aqueous solutions of H<sub>2</sub>PdCl<sub>4</sub> or Cu(NO<sub>3</sub>)<sub>2</sub>. After impregnation catalyst precursors were reduced with formaldehyde and then washed to remove chloride and nitrate ions. CuO/C catalyst was prepared by impregnation of activated carbon with aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> followed by the addition of aqueous solution of NaOH till pH reaches 8–9. The precipitate was washed with deionized water, dried in air for 24 h and calcined at 350 °C for 3 h. Bimetallic Pd–Cu catalysts with different metal loadings supported on activated carbon were prepared using the following methods: Method A: was modified electroless copper plating method widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics. Using the plating solution containing the tartrate ligands can be obtained substantially pure deposit of copper species on the surface. According to this procedure a given amount of 5%Pd/C catalyst described above was placed into freshly prepared aqueous solution containing mixture of CuSO<sub>4</sub>·5H<sub>2</sub>O, NaOH, sodium–potassium tartrate and 37% aqueous solution of formaldehyde in the molar ratios 1:6:4:18. This solution was used in the amount to obtain the required loading of copper on the bimetallic catalyst. The mixture was heated and stirred several hours, while the solution was regularly checked for the presence of copper ions in solution. Method B: The procedure was similar as in Method A, while the mixture heated at 40 °C was reduced with formaldehyde which was added separately during 1 h. This

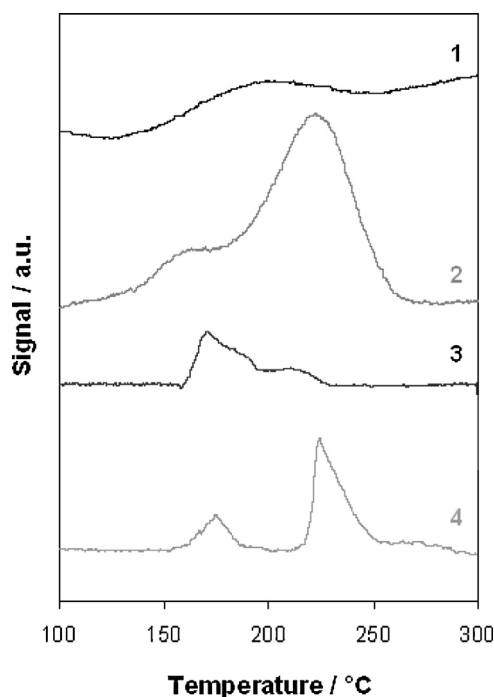
catalyst was designed 5% Pd + 10% Cu/C(sep). Method C: The procedure was similar as in Method A, while sodium–potassium tartrate in the solution was not present. Method D: 3%Pd–Cu/C catalysts with 5% and 10% loadings of copper supported on activated carbon were prepared using co-impregnation method. The samples were dried at 120 °C for 2 h, calcined at 300 °C for 5 h in flowing air and then reduced at 300 °C or 450 °C for 2 h under flowing hydrogen. The catalysts are designed 3%Pd–%Cu/C(CM300 or CM450).

### 2.3. Catalyst characterization

The surface area and pore diameters were determined from BET nitrogen adsorption measurements (Micromeritics ASAP 2020). The samples before measurement were degassed at 300 °C for 2 h. Powder X-ray diffraction (XRD) patterns were acquired on a Bruker AX S D8 diffractometer using CuK $\alpha$  radiation. Crystalline phases were identified by a comparison with the JCPDS file. The metal particle size distributions of the supported catalysts were determined by transmission electron microscopy: JEOL 1200EX microscope at accelerating voltage of 120 kV. The XPS signals were recorded using a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro focused, monochromatic Al K $\alpha$ X-ray source (1486.6 eV). An X-ray beam of 400  $\mu$ m size was used at 6 mA  $\times$  12 kV. The spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected with pass energy of 50 eV. Charge compensation was achieved with the system flood gun that provides low energy electrons ( $\sim$ 0 eV) and low energy argon ions (20 eV) from a single source. The argon partial pressure was  $3 \times 10^{-7}$  mbar in the analysis chamber. The Thermo Scientific Advantage software, version 4.87 (Thermo Fisher Scientific), was used for digital acquisition and data processing. Spectral calibration was determined by using the automated calibration routine and the internal Au, Ag and Cu standards supplied with the K-Alpha system. Temperature programmed reduction (TPR) profiles of the catalysts were obtained with Chemisorb 2720 (Micromeritics, USA) equipped with a TCD detector. The fraction of Pd exposed (CO/Pd) was estimated from dynamic CO chemisorptions measured in a pulse system equipped with TCD detector. The chemisorption analysis was performed by passing pulses of CO until a constant CO peak area was observed. The exposed metal fraction was calculated from the moles of adsorbed CO per total moles of Pd impregnated onto the catalyst.

### 2.4. Catalytic tests

Catalytic experiments were performed using procedure and analytical methods described in our previous paper [8]. For a typical reaction, 20 ml of water, 1.0 g of reactant and given amount of metal catalyst was loaded to the reactor. After sealing the reactor was several times flushed with low pressure hydrogen and then pressurized with hydrogen usually to 3 MPa (ambient temperature). The reactor was then heated to the desired temperature and the stirring speed fixed to 1500 rpm which eliminates the diffusion effects. After an appropriate reaction time the reactor was quickly cooled down, the reactor contents pour out to vial and the catalyst separated from aqueous phase by centrifugation. The quantitative determination of the liquid products concentration was done using gas chromatography by the external standard method using response factors of the corresponding standard compounds. A gas chromatography-mass spectrometry and NMR analysis were used to identify the organic compounds. GC/MS analysis of selected reaction samples has shown that in the gas phase are present only trace amounts of carbon oxides and light hydrocarbons. The yields of all reaction products were calculated on the amount of reactant charged into the reactor.



**Fig. 1.** TPR profiles of reduced catalysts: (1) 5%Pd/C; (2) 5%Pd–10%Cu/C; (3) 5%Pd–10%Cu/C (sep.); (4) CuO.

### 3. Results and discussion

#### 3.1. Catalyst characterization studies

H<sub>2</sub>-TPR was used to determine the reducibility of prepared supported catalysts. The TCD signal profiles obtained in the H<sub>2</sub>-TPR experiments with the set of catalysts are depicted in Fig. 1. The TPR profile of the reduced 5%Pd/C catalyst did not show peak at 80–300 °C which confirms the presence of metallic palladium in the catalyst. As is seen from the figure the reduction of pure CuO normally takes place in two stages, Cu(II) to Cu(I) at about 175 °C and at about 225 °C to metallic copper. Compared with the bimetallic Pd–Cu catalysts supported on active carbon the reduction of CuO or Cu<sub>2</sub>O present on these catalysts takes place at similar temperatures. However, different TPR profiles were recorded for the bimetallic 5%Pd–10%Cu catalysts supported on the same active carbon but prepared by different reduction procedures. In the reduced catalyst prepared by the electroless plating Method A copper is present mainly in Cu<sup>+</sup> oxidation stage, but in the catalyst prepared using the Method B copper is mainly in the form of CuO.

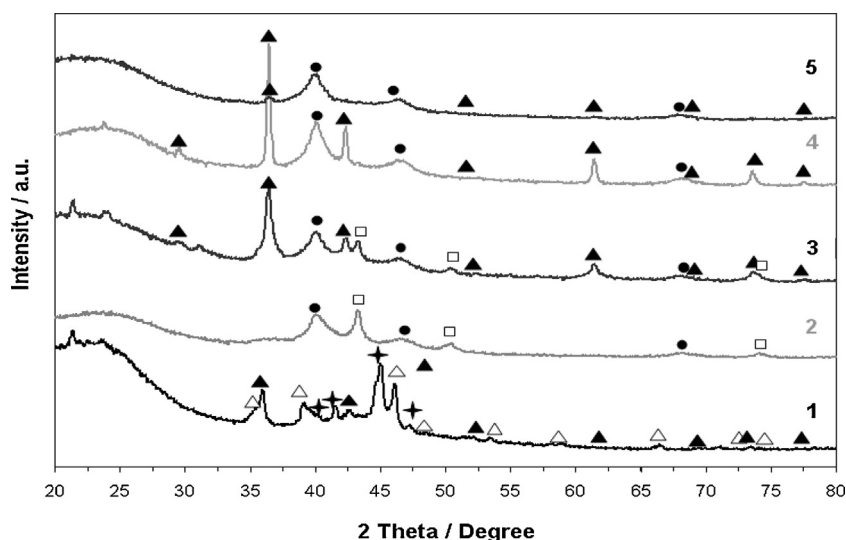
The XRD patterns of bimetallic Pd–Cu catalysts obtained using different methods of preparation and reduction are shown in Fig. 2 and the metal particle sizes determined by the Scherrer equation are in Table 1. As can be seen, microstructures of the metallic particles greatly changed depending on the method of catalyst reduction, presence of sodium–potassium tartrate during preparation and the amount of copper loading. In the XRD pattern of 5%Pd + 10%Cu/C(sep) catalyst, there are quite narrow diffraction peaks indicating the presence of particles with a well ordered structures. The peaks located at  $2\theta$  values of 40.1°, 46.6° and 68.1° are characteristic (1 1 1), (2 0 0) and (2 2 0) planes of isolated palladium crystalline, and the diffraction peaks at 43.3°, 50.4° and 74.1° to isolated metallic Cu. Since the diffraction peaks of both metals in the sample are not shifted to higher or lower angles, it indicates that no alloys phases were formed. However, the same composition of Pd–Cu catalyst, but prepared using the Method A displayed the XRD pattern with well separated diffraction peaks assigned to metallic

Pd and two characteristic peaks of Cu<sub>2</sub>O at  $2\theta$  values of 36.46° and 42.42° corresponding to reflections from (1 1 1) and (2 0 0) planes of single phase. The maximum intensity of peaks of Cu<sub>2</sub>O phase decreases when the copper loading in the catalyst decreases to 5 or 3 wt% (not shown). This trend is similar to that described in the catalytic tests. The palladium and Cu<sub>2</sub>O crystallite sizes in 5%Pd–10%Cu catalyst were 6.8 and 28.8 nm, respectively. It is important to note that in the catalyst prepared by the electroless plating Method A the XRD peaks corresponding to the metallic copper at  $2\theta$  values of 43.16° and 50.37° are absent. In contrast, the Pd–Cu catalyst prepared by the Method C displayed the XRD pattern with well separated diffraction peaks assigned to metallic Pd, and the copper which is present as a mixture of copper metal and cuprous oxide. No evidence exists for the presence of cupric oxide in the XRD pattern of the reduced catalyst. Crystallite sizes of Cu<sub>2</sub>O in this catalyst are smaller (17.7 nm) than in the same catalyst prepared by the electroless plating method. Metallic copper present on this catalyst is in the form of particles, with average sizes of 22.0 nm. The existence of different copper species were detected for supported Pd–Cu catalyst prepared by co-impregnation method, which was reduced with molecular hydrogen (catalyst 3%Pd + 5%Cu/C(CM450)). The XRD pattern of this catalyst displayed diffraction peaks barely discernible suggesting the presence of metallic particles with small sizes and/or not ordered structures. They can be attributed to the existence of different copper species, preferably CuO and Cu. Registered was also presence of Cu<sub>2</sub>O with particle sizes of 15.4 nm. The absence of metallic Pd phase indicates that Pd–Cu alloys with different composition are present in this catalyst. The peaks appearing between 39.5 and 43.5° are usually associated with the formation of Pd–Cu alloys [29].

The TEM analysis was undertaken to obtain information on distribution of the metallic particles. TEM images of the prepared bimetallic Pd–Cu catalysts are shown in Fig. 3. From the TEM pictures it is evident that the distribution of particles is homogeneous and the particles are small, which is in agreement with data obtained from XRD studies.

CO chemisorption measurements were carried out in order to measure the number of accessible Pd sites. The results obtained with the reduced catalysts are reported in Table 1. The bimetallic Pd–Cu samples show lower CO/Pd ratio compared to the monometallic sample. For the monometallic sample a CO/Pd ratio of 0.19 was measured. On the Cu-promoted catalysts prepared by electroless plating method the number of accessible surface Pd sites decreases gradually with copper loading, but this decrease is only 15% for the best catalyst. However, the decrease is significant (43–73%) for catalysts where Cu was deposited by other methods (Table 1). Since the same sample of 5%Pd/C catalyst was used for the loading of copper the higher decrease in the number of accessible Pd sites can be caused by decoration of palladium with metallic copper or by formation of other metallic species which are formed in catalysts prepared by other methods.

The chemical states of palladium and copper species on the surface of catalyst were determined by XPS analysis of 5%Pd–3%Cu/C and 5%Pd–10%Cu/C catalysts with different loading of copper prepared by the electroless plating Method A, and of the 5%Pd–10%Cu/C(sep) catalyst prepared by the Method B. The spectra of these catalysts are recorded in Fig. 4. In these catalysts the observed binding energy for Pd 3d<sub>5/2</sub> was 335.58 eV, what is in agreement with that reported in the literature [30]. In contrary to TPR data, a part of noble metal on the surface of catalysts 5%Pd–10%Cu/C and 5%Pd–10%Cu/C(sep) is found in the oxidised state Pd(II), (binding energy 337.48 eV); however, under reaction conditions (160 °C and 3 MPa of hydrogen) it is easy reduced to Pd<sup>0</sup>. Copper has two oxidation states. The samples displayed the peak (Cu 2p<sub>3/2</sub>) at 933.52 eV, which was attributed to the copper oxidation state +2. The peak at binding energy 932.31 eV is probably



**Fig. 2.** XRD patterns of reduced catalysts: (1) 3%Pd–5%Cu/C (CM450); (2) 5%Pd–10%Cu/C (sep.); (3) 5%Pd–10%Cu/C (Method C); (4) 5%Pd–10%Cu/C (Method A); (5) 5%Pd–3%Cu/C (Method A); (●) Pd<sup>0</sup> phase; (▲) Cu<sub>2</sub>O; (△) CuO; (★) Pd–Cu alloy; (□) Cu<sup>0</sup>.

**Table 1**  
Physico-chemical properties of catalysts.

Catalyst	Preparationmethod	Crystallite size (nm) <sup>a</sup>			CO/Pdratio
		Pd <sup>0</sup>	Cu <sub>2</sub> O	Cu <sup>0</sup>	
5%Pd/C	A	6.8	–	–	0.19
5%Pd + 3%Cu/C	A	6.8	n.d.	Absent	–
5%Pd + 5%Cu/C	A	6.8	16.6	Absent	0.17
5%Pd + 10%Cu/C	A	6.8	28.8	Absent	0.16
5%Pd + 10%Cu/C(sep)	B	6.8	absent	16.3	0.10
5%Pd + 10%Cu/C	C	6.8	17.7	22.0	0.07
3%Pd + 5%Cu/C (CM 450)	D	Absent	15.4	n.d.	–

<sup>a</sup> Data from XRD.

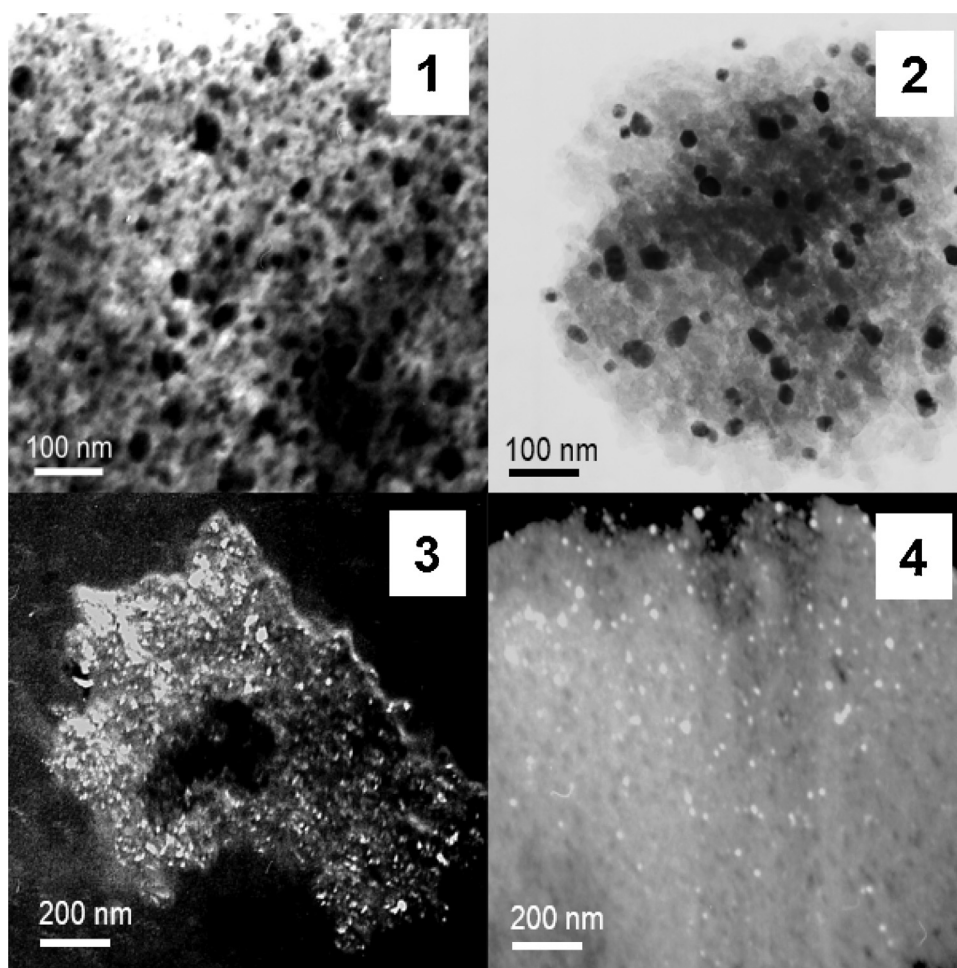
inferred to have two species Cu<sup>+</sup> and Cu<sup>0</sup>. On the basis of binding energy analysis alone it is impossible to make a distinction between them. As the XRD data revealed in the 5%Pd–10%Cu/C(sep) catalyst both these copper species are present. The comparison of intensities of the peak at binding energy 932.31 eV in the catalysts 5%Pd–3%Cu/C and 5%Pd–10%Cu/C supports that on the surface of 5%Pd–3%Cu/C catalyst is significantly lower amount of these copper species. Satellite peaks at 943.47 and 961.3 eV are evidence for CuO. Due to the differences in symmetry of CuO and Cu<sub>2</sub>O nanoparticles, the percentage of Cu(II) state is probably much lower than was observed from the XPS technique and the intensities corresponding to the Cu2p and Cu1p do not precisely reflect the ratio of them in the sample [31].

### 3.2. Catalytic activity

The catalytic data are shown in Table 2. Under these conditions the main products of furfural rearrangement were cyclopentanone, cyclopentanol and 2-cyclopentenone and the products of hydrogenation were furfuryl alcohol and tetrahydrofurfuryl alcohol. The data show that in aqueous medium monometallic 5% Pd/C catalyst is active for furfural rearrangement and produces cyclopentanone with 85.1% selectivity and 56.8 mol% yields at 66.7% furfural conversion. On the other hand monometallic Cu/C and CuO/C catalysts are pure active for furfural hydrogenation. Under comparable conditions only 14.1 and 9.1% furfural conversion was reached, respectively. Cyclopentanone was produced only over Cu/C catalyst, but with very low yield (7.2%). It is noteworthy that the activity and selectivity of Pd catalyst can be enhanced by the

addition of Cu while the change in the loading of Cu had a significant effect on the activity and selectivity. However, this effect strongly depends on the method of catalyst preparation. For the preparation of bimetallic Pd–Cu catalysts we have used (i) different procedures of deposition of copper on the pre-reduced 5%Pd/C catalyst, and the reduction of copper precursor with formaldehyde, and (ii) co-impregnation method and reduction with hydrogen. The most active and selective Pd–Cu catalysts were obtained using electroless plating method of copper deposition in the presence of tartrate carboxylate ligands (Method A). These catalysts showed high activity (78.1–98.0% conversion) and selectivity (93.6%) increasing with Cu loading (Table 2, runs 2–4). The results suggest that tartrate ligands play important role in the assembly of metal–organic framework and the formation of sufficient catalytic sites [32,33]. In this procedure operating in alkaline medium the tartrate ligands form complexes with copper (II) that are stable enough to prevent precipitation of copper(II) hydroxide. The presence of oxygen-containing ligands on the surface may stabilize the Cu precursor and prevent its reduction up to metallic copper. This is supported by the XRD patterns of these catalysts in Fig. 2. As is seen after reduction using the Method A the copper exist mainly in Cu<sup>+</sup> oxidation state as Cu<sub>2</sub>O and the diffraction peaks corresponding to metallic copper are not present. The presence of a small amount of CuO in this catalyst registered by the TPR and XPS (Figs. 1 and 4) and not by the XRD suggests that particle sizes of this phase are very small. The influence of tartrate ligands on the reduction of Cu precursor is evident from the experiment performed in the absence of tartrate salts (Method C). Using this procedure the copper precursor is reduced to highly dispersed Cu<sub>2</sub>O and metallic copper with particles diameters





**Fig. 3.** TEM images of catalysts: (1) 5%Pd–10%Cu/C (sep); (2) 3%Pd–5%Cu/C (CM 450); (3) 5%Pd–10%Cu/C (method C); (4) 5%Pd–10%Cu/C (method A).

**Table 2**  
Effect of copper and the method of Pd–Cu/C catalyst preparation on the catalyst performance Conditions: 1.0 g furfural; 20 g water; 0.010 g catalyst; 160 °C; hydrogen pressure 3 MPa; reaction time 1 h.

Run <sup>b</sup>	Catalyst	Preparation method	Conversion (%)	Yield <sup>a</sup> (mol%)				Selectivity (%)
				C <sub>PON</sub>	C <sub>POL</sub>	C <sub>EON</sub>	THFA	
1	5% Pd/C	A	66.7	56.8	0.0	0.0	2.5	85.1
2	5%Pd + 3%Cu/C	A	78.1	73.1	0.6	0.0	2.8	93.6
3	5%Pd + 5%Cu/C	A	85.9	80.9	0.6	0.0	1.4	94.1
4	5%Pd + 10%Cu/C	A	98.0	92.1	0.4	0.5	1.1	94.0
5	5%Pd + 10%Cu/C (sep)	B	100	55.6	0.0	3.3	0.6	55.6
6	5%Pd + 10%Cu/C	C	77.3	65.3	0.6	0.0	0.5	84.5
7	3%Pd + 5%Cu/C (CM 300)	D	56.2	32.7	0.6	3.6	2.0	58.2
8	3%Pd + 5%Cu/C (CM 450)	D	93.9	55.9	2.6	3.5	1.7	59.5
9	3%Pd + 10%Cu/C (CM 300)	D	100	54.0	0.4	0.0	2.8	54.0
10	10%Cu/C	– <sup>c</sup>	14.8	7.2	0	1.9	0	–
11	10%CuO/C	– <sup>c</sup>	9.1	0	0	0.7	0	–

<sup>d</sup>C<sub>PON</sub> cyclopentanone; C<sub>POL</sub> cyclopentanol; C<sub>EON</sub> 2-cyclopentenone; THFA tetrahydrofurfuryl alcohol.

<sup>a</sup> The yields calculated on furfural charged into the reactor.

<sup>b</sup> All experiments in duplicate.

<sup>c</sup> See, Catalyst preparation.

17.7 nm and 22.0 nm, respectively (Table 1). Although this catalyst is more active than monometallic Pd/C (conversion increases from 66.7 to 77.3%), cyclopentanone is produced with selectivity only about 85%. In contrast, the 5%Pd–10%Cu/C catalyst prepared in the presence of tartrate salts is much more active and selective (Table 2, run 4). These results may indicate that not only the presence of Cu<sub>2</sub>O particles but also their size should influence the selectivity of reaction. This suggestion supports observations reported over Pt,

Rh, Ru and Co catalysts that larger particles gave higher selectivity towards alcohols in hydrogenation of aldehydes [34–36]. Nagaraja et al. assumed [37] that the larger Cu particles in Cu/MgO catalysts prevent the ring hydrogenation in furfural, and hence increase the selectivity towards furfuryl alcohol.

For the preparation of active and selective bimetallic Pd–Cu catalysts important is not only presence of tartrate ligands but also the procedure of reduction of copper precursor. As is evident from

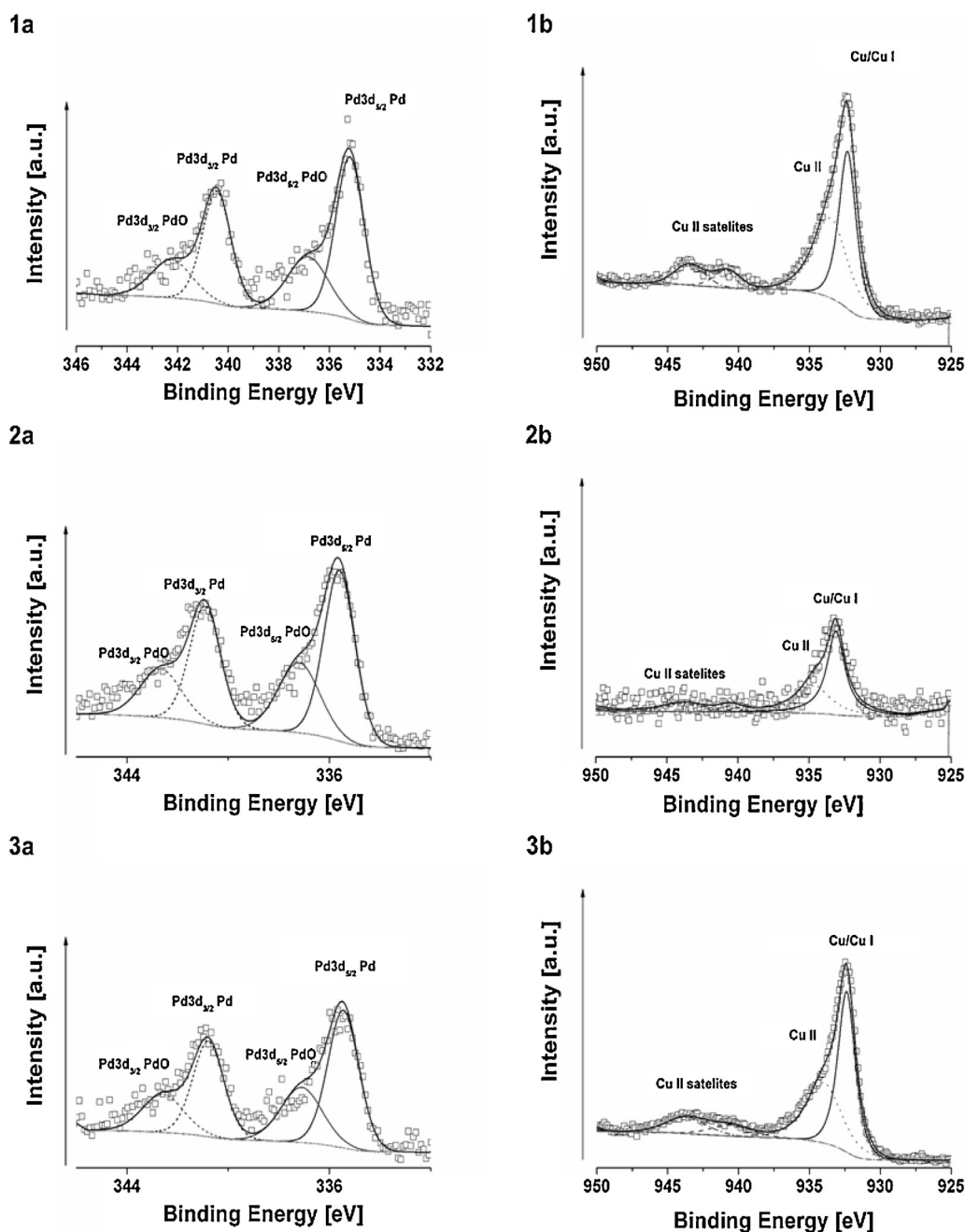


Fig. 4. XPS Pd 3d (a) and Cu 2p (b) spectra of (1) 5%Pd–10%Cu/C; (2) 5%Pd–3%Cu/C and (3) 5%Pd–10%Cu/C (sep.) catalysts.

the catalytic tests (Table 2, run 5), the reduction of Cu precursor according to the Method B leads to the formation of highly active (complete furfural conversion) but less selective catalyst of furfural rearrangement (only 55.6% selectivity). As shown in the XRD pattern in this catalyst are present diffraction peaks corresponding to metallic palladium and metallic copper, while the peaks characteristic to  $\text{Cu}_2\text{O}$  phase are absent. These findings indicate that the highly active and also selective bimetallic Pd–Cu catalysts must contain both, metallic Pd and  $\text{Cu}_2\text{O}$  particles, as revealed the TPR, XRD and XPS spectra. About 15% decrease in the number of accessible surface Pd sites by loading of 10 wt% of copper, determined by CO chemisorption measurements suggests that Pd is only partly decorated with  $\text{Cu}_2\text{O}$  particles. These particles are mostly located near Pd particles and due to the close contact the Cu particles are stabilized in a lower oxidation state. The surface composition and

thus the chemical reactivity of supported bimetallic Pd–Cu catalysts can be tuned by variation of the ratio of both metal precursors, and by the method of their deposition and reduction during catalyst preparation.

The best catalytic performance for the furfural rearrangement was obtained using 5%Pd–10%Cu/C catalyst prepared by the electroless plating Method A. With less copper and as was indicated from the XRD data, by the lower possibilities of forming  $\text{Cu}_2\text{O}$  sites participating on the rearrangement reaction, the catalytic performance of bimetallic catalysts decreases. Bimetallic Pd–Cu/C catalysts with 5 and 10% of copper loading prepared by coprecipitation method and reduced with hydrogen at 300 °C or 450 °C (Method D) displayed lower selectivity to cyclopentanone than those reduced with formaldehyde (Table 2, runs 7–9). High conversions of furfural were reached using catalysts reduced at

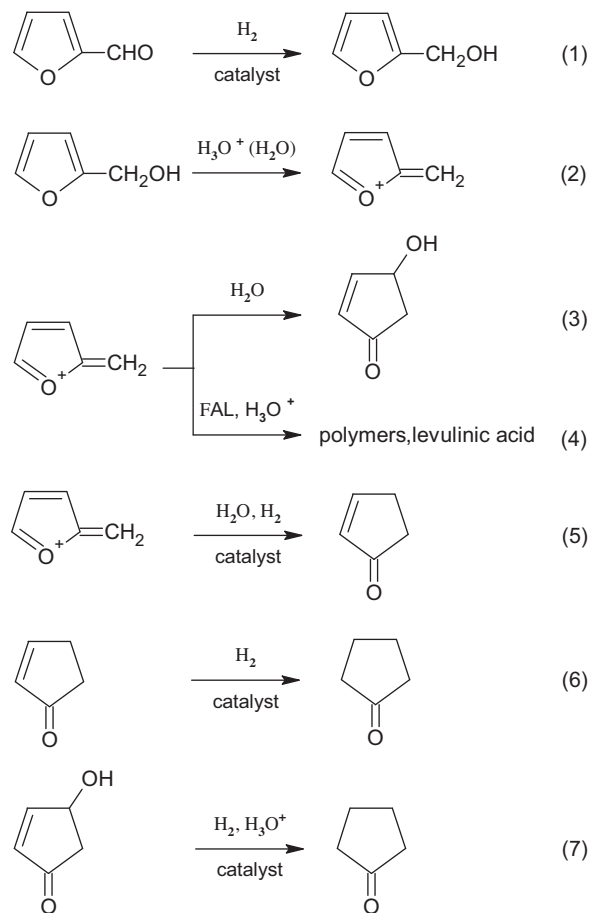
higher temperature (450 °C) or doped with higher amount of copper precursor. However, the selectivities remain low, only about 54–59.5%. A comparison of the XRD pattern in Fig. 2 reveals that after reduction, CuO and Cu phases and Pd–Cu alloys with different composition are present in the catalyst.

The above mentioned results suggest that the main differences between samples with different Cu loadings and the different methods of their preparation are attributed to changes in metal containing phases and particle sizes over the catalyst surface. However, the way in which the Cu additive modifies the properties of Pd–Cu/C catalysts is not yet fully elucidated and needs further investigation. As the results have shown the catalytic activity and selectivity of furfural rearrangement are highly sensitive to the surface composition. In the most active and selective Pd–Cu catalyst are according to TPR and XRD observations present on the catalyst surface preferably metallic Pd and Cu<sub>2</sub>O phases. The presence of high concentration of Cu<sup>+</sup> phase and absence of Cu<sup>0</sup> phase after reduction indicates that Cu<sup>+</sup> must be involved in the catalytic cycle.

In the literature controversies exist regarding the catalytic mechanism associated with active sites of Cu<sup>+</sup> species [39]. Monnier et al. [28] suggested that Cu<sup>+</sup> is responsible for CO chemisorption during methanol synthesis. Lin et al. [38] reported that Cu/SiO<sub>2</sub> catalyst with the largest Cu<sup>+</sup> surface area and the highest Cu<sup>+</sup>/(Cu<sup>+</sup> + Cu<sup>0</sup>) ratio exhibits the best catalytic activity for dimethyl oxalate hydrogenation to ethylene glycol. Wang et al. [40] found that reduction temperature influences the Cu<sup>0</sup>/Cu<sup>+</sup> ratio and catalytic performance of Cu/SiO<sub>2</sub> catalyst. Lee et al. [41] applied Cu<sub>2</sub>O nanoparticles as catalysts for reduction of 4-nitrophenol. Rao et al. [42] proposed that Cu<sup>+</sup> species function as active sites for furfural and crotonaldehyde hydrogenation. However, the way in which the Cu<sup>+</sup> modifies properties of metallic catalysts is not yet fully elucidated and is a matter of debate in the literature [43]. To understand the surface structure of catalyst and the catalytic processes the adsorption of CO molecule on the Cu<sub>2</sub>O (1 1 1) surface in gas phase has been studied [44,45]. As the studies have shown the chemical characteristics in liquid phase environment are different from those in gas phase. The interaction of solvent molecules with Cu<sub>2</sub>O (1 1 1) surface causes that solvent molecules, e.g. water, basically contribute for the enhancement of CO interaction with Cu<sub>2</sub>O (1 1 1) surface, in which Cu<sub>2</sub>O (1 1 1) shows higher catalytic performance for C–O bond activation [45].

On the Pd (1 1 1) surface the preferential adsorption mode of furfural is a flat adsorption promoted by furyl ring which results in greater elongation of the carbonyl bond [26,46]. As the authors stated, the interaction of aldehyde with the metal surface significantly reduces the presence of Cu in the catalyst. The interaction of furfural with the Cu surface is via the carbonyl oxygen and the furyl ring is not strongly bound to the surface [47]. Rao et al. [48] used two-site Langmuir–Hinshelwood model to describe the roles of Cu<sup>0</sup> and Cu<sup>+</sup> sites in the hydrogenation of furfural to furfuryl alcohol. In this model they proposed that Cu<sup>0</sup> sites are responsible for dissociative adsorption of H<sub>2</sub> and the Cu<sup>+</sup> sites for furfural adsorption. Also Hernandez et al. [49] proposed that over SBA–Cu catalysts the presence of both Cu<sup>+</sup> and Cu<sup>0</sup> species on the surface is responsible for the high activity and selectivity towards furfuryl alcohol.

We suggest that in our Pd–Cu/C catalysts exhibiting the best performance, on the catalyst surface may be present monometallic Pd<sup>0</sup> sites and closely interacting bimetallic Pd<sup>0</sup>–Cu<sub>2</sub>O catalytic sites. Furfural undergoes reversible molecular adsorption on Cu<sub>2</sub>O surfaces and bonds to the Cu<sup>+</sup> cation via the oxygen lone pair of the molecule, accompanied by a transfer of electrons to the surface of Cu<sup>+</sup> cation. The polarized carbonyl group facilitates hydrogen transfer from the adjacent Pd–H sites. The interaction of Cu<sub>2</sub>O surface with the solvent molecules, i.e. water, causes that water probably contributes for the enhancement of furfural interaction with Cu<sub>2</sub>O surface. Providing that Pd<sup>0</sup> sites are present to



**Scheme 1.** Proposed mechanism of furfural conversion to cyclopentanone.

dissociate hydrogen, hydrogenation of  $\text{C}=\text{O}$  group in adsorbed species created on Cu<sup>+</sup> sites readily occurs. An appropriate formation and distribution of sufficient mono- and bimetallic sites and an optimal ratio between these sites are necessary for high activity and selectivity.

### 3.3. Mechanism of cyclopentanone formation

Scheme 1 depicts proposed mechanism of catalytic rearrangement of furfural to cyclopentanone. The mechanism was formulated based on our previous experimental studies [8,9,50] conducted in the absence and presence of various types of heterogeneous catalysts with furfural, furfuryl alcohol and some stable intermediates as reactants.

In the first step of reaction, the active Cu<sup>+</sup> sites on the catalyst surface attack the lone pair of aldehydic group facilitating hydrogen transfer from the adjacent Pd–H sites. Selective formation of furfuryl alcohol (FAL) in this stage is a key step in the rearrangement reaction and its yield directly affects the yield of cyclopentanone. As described above in our most active and selective catalysts metallic copper is practically not formed during catalysts preparation. Therefore the catalytic centers for furfural hydrogenation are mainly Pd<sup>0</sup> and Cu<sup>+</sup> species. Pd atoms act as sites for hydrogen uptake, dissociation, and spillover onto the surrounding Cu<sup>+</sup> species interacting with adsorbed furfural. However, hydrogen adsorbed on Pd can also cause consecutive hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol, leading to lower selectivity. It is evident from experiments performed with monometallic Pd/C catalyst (Table 1, run 1 and lit. [9]) that depending on the catalyst loading and hydrogen pressure furfuryl alcohol is hydrogenated also

to tetrahydrofurfuryl alcohol. The presence of  $\text{Cu}^+$  species influences that with more copper in the catalyst and therefore more possibilities forming  $\text{Cu}^+$ –Pd sites, less isolated Pd sites are available for subsequent hydrogenation of formed furfuryl alcohol. This is in agreement with the observed catalytic results obtained using Pd–Cu/C catalysts, having 3, 5 and 10 wt% loading of copper; all prepared by electroless plating method (Table 2, runs 1–4). Slight decrease of accessible surface Pd sites in these catalysts by deposition of Cu is compensated by the creation of catalytically active  $\text{Cu}^+$ –Pd centers providing higher furfural conversion and cyclopentanone yield. Hence, combining Pd and  $\text{Cu}_2\text{O}$  nanoparticles causes a substantial increase in reaction rate. Significantly lower yields of cyclopentanone and carbon balance were obtained using Pd–Cu/C catalysts containing 5 or 10 wt% of copper, prepared by others procedures (Table 2 runs 5–9). In these catalysts copper is present in the form of metallic copper, CuO or Pd–Cu alloys, as revealed the XRD data (Fig. 2, Table 1). Over these catalysts active centers for furfural hydrogenation are also formed, but as is discussed below these centers are catalytically less active for reactions proceeding in the second step.

In the second step of reaction proceeding in water at temperatures 140–160 °C the formed furfuryl alcohol can be converted by different pathways [50]. However, in these pathways the reaction starts by protonation of FAL with hydrogen protons formed by auto-dissociation of water [51]. The formation of the FAL oxycation species (Scheme 1) at the reaction temperatures is thermodynamically more favourable [52]. In the presence of active Pd–Cu/C catalysts the cooperation between  $\text{Pd}^0$  and  $\text{Cu}_2\text{O}$  sites probably promotes stabilization of oxycation species, and thus prevents their undesired acid catalysed conversions to 4-HCP and polymers by Reactions (3) and (4). Subsequent rearrangement of stabilized cationic species through cascade reactions (Scheme 2) lead to unstable intermediates which entails first hydrogenation of the  $\text{C}=\text{O}$  with chemisorbed hydrogen and after dehydration gives relative stable and detectable 2-cyclopentenone (Reaction (5)). After hydrogenation (Reaction (6)) 2-cyclopentenone is converted exclusively to cyclopentanone, because its consecutive hydrogenation to more stable cyclopentanol is inhibited by the presence of polymers of furfuryl alcohol created on the catalyst surface [53].

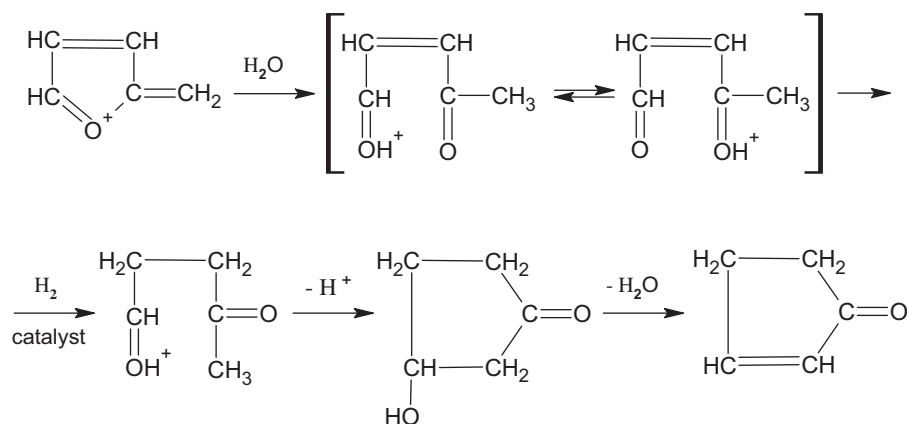
However, if the metal catalyst is less active or the reaction is performed at low concentration of hydrogen in the liquid phase (e.g. at low partial hydrogen pressure or/and at insufficient mixing of liquid phase) the formed FAL oxycation is by Reaction (3) rapidly converted (i) to 4-hydroxy-2-cyclopentenone (4-HCP), and (ii) by the attack with other FAL molecules to oligomers and polymers, or (iii) in the presence of strong acids to the ring opening products, e.g. levulinic acid [9]. Our previous studies [8] and also results of other authors [10] shown that under reaction conditions 4-HCP is easy converted to cyclopentanone. On the bases of these results some authors [10–12] proposed the mechanism involving 4-HCP as the main reaction intermediate. Although this pathway cannot be fully excluded it seems that it is not the dominant pathway for furfural rearrangement conducted in kinetic regime and in the presence of highly active and selective metal catalyst. Against the pathway via 4-HCP are the following experimental observations: (a) in many reaction mixtures was detected the presence of 2-cyclopentenone, but not more stabile 4-HCP, (b) when under comparable reaction conditions 4-HCP alone was hydrogenated the maximum cumulative yield of cyclopentanone and cyclopentanol was 73 mol% [8,10], (c) in water at temperatures about 150–160 °C furfuryl alcohol is converted to 4-HCP with the maximal yield 60–65 mol%, and other part of furfuryl alcohol is converted to polymeric products, what results in low carbon mass balance [50]. Taking into account these facts and the assumption that the conversion of furfural to cyclopentanone proceeds only through 4-HCP, than the yield of cyclopentanone should not be higher than 60–65 mol%. It means

that the reactions (3), (4) and (7) play important role, and besides 4-HCP as the main intermediate also high amount of by-products (oligomers and polymers) is formed.

### 3.4. Influence of mass-transfer effects

As is presented in Table 3 run 3, using very low concentration (1 wt%) of 5%Pd–10%Cu/C catalyst it is possible to achieve 92.1 mol% yield of cyclopentanone during short reaction time (1 h). These data were obtained at an impeller speed 1500 rpm, which ensured that the gas–liquid and liquid–solid mass-transfer resistances are eliminated. The study of furfuryl alcohol rearrangement in water has shown [9] that in kinetic regime crucial parameters affecting the selectivity to cyclopentanone are concentration of heterogeneous metal catalyst and hydrogen pressure. Table 3 demonstrates the effect of catalyst concentration, reaction parameters and speed of mixing on the process of furfural conversion to cyclopentanone. As is evident from these results optimal concentration of catalyst and hydrogen pressure are required to obtain high yield of cyclopentanone. However, this is valid only under conditions when the mass-transfer effects are eliminated. If it is not achieved (e.g. at lower speed of mixing) despite using very active catalyst the selectivity to cyclopentanone sharply decreases (Table 3, run 4). Such behaviour can be explained considering that furfuryl alcohol formed by hydrogenation of furfural is subsequently converted through parallel reactions. One reaction pathway catalysed by metals is the sequence of consecutive reactions (Scheme 2), simply depicted as Reactions (5) and (6). The second parallel pathway is catalysed by hydrogen ions formed by auto-dissociation of water. This pathway involves irreversible conversion of furfuryl alcohol to 4-HCP (Reaction (3)) and polymers (Reaction (4)), followed by metal catalysed conversion of 4-HCP to cyclopentanone (reaction (7)). Since the concentration of hydrogen ions is dependent only on the dissociation constant of water [51], the rate of protonation of FAL (Reaction (2)) at constant temperature is the same. Thus, the proportion between these two reaction pathways depends on the ratio of rates of acid-catalysed Reactions (3) and (4), and the rate of Reaction (5) catalysed by metal catalyst. The rate of reaction (3) is monomolecular (water is in large excess) and depends only on the temperature. However, the rate of Reaction (5) is essentially influenced also by the concentration of molecular hydrogen dissolved in the liquid phase; i.e. by the hydrogen pressure and the gas–liquid interface area (by stirrer speed). The catalyst enhances the rates of transformation of the oxycation species to 2-cyclopentenone via the cascade reactions (Scheme 2), and probably may stabilize the ionic species created on its surface. Hence, the rate of Reaction (5) is responsible for reaching very high selectivity to cyclopentanone. If this rate is slower than the rate of Reaction (3), i.e. the intermediate is 4-HCP, the selectivity of reaction is significantly lower. This suggestion clearly supports experiments performed at low catalyst loading, low hydrogen pressure and at insufficient mixing of reactants (Table 3). Less than 75% carbon mass balance observed in these runs also proves that important part of reactant is transformed by Reaction (4) to oligomeric and polymeric products. However, if hydrogenation reaction was performed at optimal conditions in kinetic regime the yield of cyclopentanone reached 92.1 mol% (Table 3, runs 3 and 4). Another evidence that the pathway through 4-HCP is significantly less selective is given by experiments performed with furfuryl alcohol. In these runs the liquid phase was during the heating period (i) rigorously mixed or (ii) mixed slowly and only after reaching the desired reaction temperature the speed of stirrer 1500 rpm was set up. The results in Table 3 (runs 5–8) showed that if the liquid phase was during the heating period mixed slowly, i.e. the concentration of hydrogen in the liquid phase was low; in accordance with the proposed mechanism furfuryl alcohol was mostly converted to 4-HCP through less selective reaction (3).





**Scheme 2.** Possible pathway for the conversion of oxycation to cyclopentenone.

**Table 3**  
Effect of reaction conditions on the performance of 5% Pd–10%Cu/C catalyst prepared by method A Conditions: 1.0 g furfural; 20 ml water; reaction temperature 160 °C.

Run	Catalyst (g)	Hydrogen pressure (MPa)	Reaction time (min)	Conversion (%)	Yield <sup>a</sup> (mol%)			
					C <sub>PON</sub>	C <sub>POL</sub>	C <sub>EN</sub>	THFA
1	0.003	1.0	30	34.4	3.9	0.0	5.8	0.0
2	0.03	1.0	60	96.1	67.2	0.0	4.7	5.2
3	0.01	3.0	60	98.0	92.1	0.4	0.5	1.1
4 <sup>c</sup>	0.01	3.0	60	98.5	64.5	0.9	0.6	0.0
5 <sup>b</sup>	0.01	2.5	60	100	66.3	11.5	0.0	0.0
6 <sup>b,c</sup>	0.01	2.5	60	100	57.3	5.4	0.0	0.0
7 <sup>b</sup>	0.01	1.0	30	100	70.8	0.0	10.9	1.3
8 <sup>b,c,d</sup>	0.01	1.0	120	100	43.1	0.0	9.9	1.8

<sup>a</sup> The yields calculated on furfural charged into the reactor, the speed of stirrer 1500 rpm.

<sup>b</sup> Instead of FA was used furfuryl alcohol.

<sup>c</sup> Stirrer speed 400 rpm; Runs 7 and 8 were performed using catalyst G-134 A.

<sup>d</sup> Also 8.1% 4-hydroxy-2-cyclopentenone was detected.

Despite subsequent increase of the stirrer speed the cumulative yield of cyclopentanone and cyclopentanol was only 62.7 mol% (run 6). However, when the speed of stirrer was continuously fixed to 1500 rpm, i.e. the sufficient concentration of hydrogen in the liquid phase was present also during the heating period, the Reaction (5) was dominant resulting in essentially higher cumulative yield of cyclopentanone and cyclopentanol (77.8 mol%, run 5). The same effect on the yield of desired product was observed using less selective nickel catalyst (Table 3, runs 7 and 8). The presence of 8.1% of 4-HCP determined in the run 8 also supports the validity of the proposed reaction mechanism.

The high concentration of hydrogen in the liquid phase accelerates not only the rate of Reaction (5), but also hydrogenation of furfural to furfuryl alcohol (Reaction 1). The kinetic study has shown that at temperatures about 160 °C furfuryl alcohol in aqueous solution is unstable and is very quickly converted to 4-HCP and oligomers [50]. Since the presence of furfuryl alcohol in reaction mixtures of furfural hydrogenation to cyclopentanone never been detected, it indicates that even at high concentrations of hydrogen in the liquid phase the rates of consecutive reactions of furfuryl alcohol, preferably via Reaction (5), must be much higher than the rate of furfural hydrogenation to furfuryl alcohol.

#### 4. Conclusions

In this contribution, we presented the study of Pd–Cu/C bimetallic catalysts and the influence of copper on the catalytic behaviour in furfural conversion to cyclopentanone. Surface compositions of Pd–Cu/C catalysts were characterized by means of TPR, XRD, TEM, XPS and CO chemisorption studies. Catalytic tests were performed in batch reactor under conditions where diffusion of reactants does

not influence the chemical reaction. For the preparation of bimetallic Pd–Cu catalysts were used (i) different procedures of deposition of copper on the pre-reduced 5%Pd/C catalyst and the reduction of copper precursor with formaldehyde, and (ii) co-impregnation method followed by reduction with hydrogen. The most active and selective Pd–Cu catalysts were obtained using electroless plating procedure of deposition of copper in the presence of tartrate carboxylate ligands. It is an alternative and promising way to deposit uniform metal nanoparticles onto the surfaces of porous solid supports. As the XRD, TPR and XPS data revealed in catalysts prepared by this method beside metallic palladium with the particle sizes 6.8 nm the copper exist in  $Cu^+$  oxidation state as  $Cu_2O$ , while metallic copper is almost absent. We assume that in these catalysts the  $Cu^+$  sites play important roles in binding and activating the  $-C=O$  group in furfural. An appropriate  $Pd^0$  and  $Cu^+$  distribution is presumed to be a key in gaining excellent catalytic activity. The conversion and selectivity variations are discussed on the basis of structural differences of metallic phases in Pd–Cu catalysts. Under optimal conditions (160 °C, 3 MPa of hydrogen, 1 wt% of catalyst with respect to furfural) where mass-transfer effects are eliminated furfural conversion about 98% and 92.1 mol% cyclopentanone yield were obtained throughout 1 h of reaction.

The mechanism of furfural conversion in water as a solvent was formulated and experimentally verified. A key step in the mechanism influencing the yield of cyclopentanone is the selective formation of furfuryl alcohol from furfural. A very important role plays also the concentration of hydrogen in the liquid phase. At high concentrations of hydrogen are suppressed the rates of undesired acid catalysed reactions of oxycationic species. They are created from furfuryl alcohol by the attack with hydrogen ions formed by auto-dissociation of water.

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